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Adsorption of Zinc Using the Activated Carbon Prepared from Coconut Coir

by

Ain Nadhila Binti Awang

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Universiti Teknologi PETRONAS

Bandar Seri Iskandar

31750 Tronoh

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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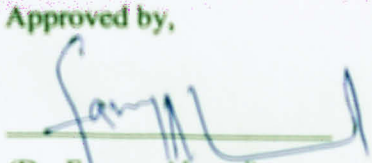
Approved by,



(Dr. Farooq Ahmad)
DR FAROOQ AHMAD
Lecturer
Chemical Engineering Department
Universiti Teknologi PETRONAS

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

JULY 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

AIN NADHILA BINTI AWANG

ABSTRACT

In this study, the removal of zinc ions [Zn (II)] from aqueous solutions by using agricultural by-product of coconut coir for activated carbon preparation was investigated. The effects of initial solution pH, initial metal ion concentration and amount of adsorbent on the adsorption process were also examined. The different kinetic modeling analysis of the Elovich, pseudo-first order, pseudo-second order, intraparticle diffusion, mass transfer and intraparticle diffusivity equations will be used to analyze the kinetic data for Zn (II) ion adsorption. The kinetic parameters including rate constant are determined at different initial metal ion concentration, pH and the amount of adsorbent. The Langmuir and Freundlich adsorption isotherm models are used to describe the experimental data and Langmuir model showed a better correlation coefficient. The coconut coir was found to be a metal adsorbent as effective as activated carbon.

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ABBREVIATIONS AND NOMENCLATURE

AC	=	Activated Carbon
AAS	=	Atomic Adsorption Spectrophotometer
FBAU	=	Fived Bed Activation Unit
XRD	=	X-ray Diffraction
TGA	=	Thermogravimetric Analysis
SEM	=	Scanning Electron Microscope
EDX	=	Energy Dispersive X-ray Spectroscopy
FTIR	=	Fourier Transform Infrared Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The use of coconut coir, obtain from agricultural by-products, for removing Zn (II) from the aqueous solution has been investigated. Considerable research has been conducted by using adsorption technique. The use of coconut coir which can be obtained from local by-products in Malaysia found as a potential and low-cost natural bio-adsorbent for the preparation of activated carbon. This study also focuses on the influences of solution pH, amount of adsorbent and initial metal ion concentration of coconuts coir using batch kinetic and adsorption experiments. The rate kinetics and equilibrium parameters were determined to understand the mechanism of adsorption. Adsorption isotherm models and thermodynamic parameters were also investigated to know the adsorption characteristics.

Adsorption is the most popular technique to remove the heavy metals. In addition, adsorption onto activated carbon is considered as an effective technique that was extensively used in the last few years and also demands for a better quality of treated water effluent including toxicity reduction. The performance of the natural adsorbent will be measured by the capability of removing Zn (II) from its aqueous solution. The analysis will be done using an Atomic Adsorption Spectrophotometer. In this setting, the use of low-cost materials for recovering heavy metals from contaminated industrial effluent has also emerged as a potential alternative method to conventional technique. For example, some of the non-conventional low cost adsorbents recently used for removal of heavy metals are hazelnut shell, apple residues, banana pith, tree leaves, orange waste, grape stalk waste and rice polish.

1.2 Problem Statement

The increase in environmental pollution caused by heavy metals is of great concern because of their carcinogenic properties, their non-biodegradability and bio-accumulation. The presence of heavy metals such as cadmium, zinc, cooper, lead, nickel etc, over the permissible concentrations in the environment can be detrimental to living species and may cause serious illness to the public. In most aquatic systems, the elimination of heavy metals from water and wastewater is extremely important for public health. Zinc is considered as an essential element for life and acts as a micronutrient when present in trace amounts. The maximum acceptable concentration of heavy metals in drinking water is 5.0mg/L. Otherwise, it cannot be metabolized by the human body and therefore it accumulates in the body. Heavy metal toxicity can cause our mental functions, energy, nervous system, kidneys, lungs and other organ functions to decline.

The main source of zinc in waste water is discharging waste streams from metals, chemicals, pulp and paper manufacturing processes, steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscous rayon yarn and fibber production etc. Conventional methods for heavy metals removal such as chemical oxidation, reduction, ion exchange, filtration precipitation, solidification, electrolytic recovery, solvent extraction, and adsorption on activated carbon are some of the physicochemical waste water treatment processes. Application of such methods however is sometimes restricted because of technical or economical constraints.

Among various treatment technologies, activated carbon adsorption is commonly used due to its porous surface structure, which provides it with a high surface area, harmlessness to the environment and ease in operation. However, the high cost of activated carbon has led to the development of new adsorbents with similar characteristics, but lower costs. Therefore, there is a need to search into alternatives to investigate low-cost, effective and economical adsorbents.

1.3 Objectives

1) To study on the adsorption process for zinc removal from the aqueous solution by using coconuts coir as adsorbent.
2) To prepare the activated carbon from natural by-product which is coconut coir.
3) To understand the adsorption characteristics such as mechanism and kinetics of adsorption.
4) To study on the characteristics of the produced activated carbon by using FTIR, TGA, XRD, SEM & EDX.
5) To analyze the effect of pH, amount of adsorbent and initial metal ion concentration on the adsorption process.
6) To explore the feasibility and effectiveness of the activated carbon prepared from coconuts coir for zinc removal.

1.4 Scope of Study

The whole project would start with the knowledge gathering and theoretical studies. Next stage was carried out the experiments to correlate the theoretical knowledge with practices. The experiments on the preparation of the activated carbon and adsorption technique are implemented to remove zinc. Characterization of the activated carbon obtained in the optimal condition was conducted by using the following technique which are FTIR, SEM, EDX, TGA and XRD.

Tools and equipments are identified and familiarized prior to the laboratory tests to avoid malfunctioning of the system. Accuracy of equipments used in the tests also will be checked in order to get accurate results. Results obtained from the laboratory tests have been analyzed and interpreted. Further research and development would be continuously carried out to ensure satisfactory results are achieved. A recommendation will be made based on the findings of this study regarding the applicability of coconut coir in adsorption process of heavy metal.

CHAPTER 2

LITERATURE REVIEW

2.1 Zinc

Zinc is the metallic chemical element which the symbol Zn and atomic number of 30. It is the first-row transition metal of the group 12 of the periodic table. Zinc is one of the most common elements in the earth's crust. It is also an essential element for all living things. Pure zinc is a bluish-white and shiny metal. Powdered zinc is explosive and can burst into flames if stored in a damp place. Because it is an element, zinc does not degrade nor can it be destroyed. Most of the common compound of zinc is white (colorless when liquid). Zinc has many commercial and industrial uses. Metallic zinc is used to coat iron and other metals to prevent rust, and it is also used in dry cell batteries. Zinc is mixed with other metals to form alloys such as brass and bronze, and pennies are made from a copper-zinc alloy. Zinc is also combined with other elements such as chlorine, oxygen, and sulfur to form zinc compounds used to make white paints, ceramics, rubber, wood preservatives, dyes, and fertilizers.

Zinc is found throughout the environment in air, soil, and water, and it is present in all foods. It can be released by natural processes, but most results from human activities. Releases to air, water, and soil are common in areas where ores are mined, processed, and smelted for zinc. Zinc can be releases to the atmosphere during the production of steel and burning of coal or waste. Surface water can be impacted by discharges of metal manufacturing and chemical industry wastes, and also by run-off following precipitation on soils high in zinc. The U.S. Environmental Protection Agency (EPA) has stated that adequate information to evaluate the carcinogenicity of zinc is not available. However, no studies exist that indicate zinc causes cancer in humans [1].

2.2 Adsorption

Adsorption process has been reported to be superior alternative for the removal of heavy metals from their aqueous solutions. In fact, this is the mechanism used in nature to free the environment from most of the pollutants and also technique for water re-use in terms of initial cost, simplicity design, ease of operation and insensibility toxic substances[2].

Adsorption is the process of accumulating substances that are in solution on a suitable interface. In other hand, adsorption is the process by which Activated Carbon removes substances from water. Defined, adsorption is "the collection of a substance onto the surface of adsorbent solids." It is a removal process where certain particles are bound to an adsorbent particle surface by either chemical or physical attraction. In order to properly design and operate fixed bed adsorption process, the removal mechanism must be understood. Parameter such as pH of the adsorbate solutions has been identified as the single most important parameter governing adsorption on different adsorbents.

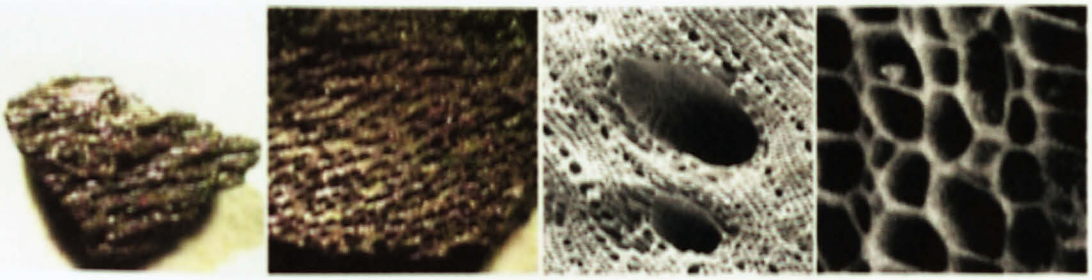
In the sorption of metal cations the pH of the solution is the prominent factor. Moreover, zinc speciation is pH dependent. Then, the uptake mechanism can be affected according to pH of the feed solution [3]. Such parameters can be investigated through the adsorption isotherm and kinetics experiments such as the effects of initial solution pH, initial metal ion concentration and amount of adsorbent on the adsorption process. The characteristics of adsorption behavior of activated carbon are generally inferred in terms of both adsorption kinetics and equilibrium isotherm. Therefore, to study both the adsorption kinetics and equilibrium, it is important to understand the adsorption mechanism. The Langmuir and Freundlich adsorption isotherm models are used to describe the experimental data and Langmuir model showed a better correlation coefficient [5]. There are different kinetics models to be used to analysed the adsorption kinetic data of Zn (II) ion such as the pseudo-first order, pseudo-second order, Elovich, mass transfer and intraparticle diffusion [8].

2.3 Activated carbon as an adsorbent

The most widely used adsorbent for this purpose is activated carbon, but commercially available activated carbons are expensive and so they may not be economical for wastewater treatment. Other untreated low-cost adsorbents often have low adsorption capacities; therefore their removal efficiencies are poor. If an activated carbon with high adsorption capacity for wastewater treatment purpose can be produced from low-cost or waste materials, then its use as an adsorbent should be economical.

Activated carbon is the most popular adsorbent for the adsorption process since it has high adsorption capacity. The adsorption capacity of activated carbon depends not only on its surface area, but also on its internal pore structure, surface characteristic and the presence of functional group on pore surface. Internal pore structure and surface characteristic play an important role in adsorption processes and depend both on the precursor used and method of preparation. In this study, Granular Activated Carbon is used because it has an extensive pore structure which provides an enormous amount of surface area for each particle of material. For example, the surface area available in one pound of granular activated carbon is equivalent to six football fields [9].

Figure 1: Close ups of Activated Carbon Surface and Pores. (Magnification increases left to right)



Coconut is one of the famous fruit commodities in Malaysia and direct discharge of these solid wastes (coconut coir) will cause the environmental problems. Although there are many studies in the literature concerning to the preparation of activated carbon, there is no details information and research for the production and utilization of activated carbon from coconut coir for heavy metals removal.

2.4 Adsorption Isotherms

An adsorption isotherm describes the relationship between the amount of metal adsorbed and metal ion concentration remaining in solution. In addition, isotherms are empirical relations which are used to predict how much solute can be adsorbed by activated carbon. The three most well known isotherms are the Freundlich, Langmuir and Linear. The equation parameters and the underlying thermodynamic assumptions of the experiments often provide some insight into both the adsorption mechanism and the surface properties and affinity of the sorbent. The equilibrium data are analyzed in accordance with the Langmuir and Freundlich sorption isotherms. These isotherms allow describing adsorption phenomena of metals from aqueous solution onto soil sample [3].

2.4.1 Freundlich isotherm

Freundlich isotherm which assumes that different sites with several adsorption energies are involved, is expressed by

$\log C_s = \log KF + n \log C_e$

Where KF is the Freundlich distribution coefficient related to the total adsorption capacity of the solid, and n is a nonlinear constant.

2.4.2 The Langmuir isotherm

Expressed by;

$$\frac{C_e}{C_s} = \frac{C_e}{C_s^{max}} + \frac{1}{C_s^{max} b} \quad \text{with } C_s = K_d C_e$$

where Kd is the distribution coefficient that characterizes the affinity of the metal for the sorbent, Cs max is the maximum adsorption capacity of the solid corresponding to complete monolayer coverage, Ce is the measured concentration (μmol L−1) of metal in solution when the equilibrium is reached, Cs is the measured adsorption per unit weight of solid (μmol g−1), and b represents the Langmuir bonding term (L μmol−1) related to the adsorption energy [7].

2.5 Adsorption experiments

The bio-adsorbent was added to glass flasks containing a known amount of metal solution. Next, the 100 ml of metal ion solution will be shaken in a constant temperature shaker at 150 rpm for a given time and then the suspensions will be filtered through a 0.45 μm syringe filter. The filtrate was analysed using flame atomic absorption spectrophotometer with air-acetylene flame. The pH of the liquid is adjusted with dilute HCl and NaOH solution. The experiments will be carried out by varying the initial metal ion concentration, amount of adsorbent and the pH. Adsorption rates are measured according to predefined procedure with both metal ion concentration ranging from 5.0 to 50 mg/L. The metal ion concentration is calculated using the general definition.

$$q_t = \frac{(C_o - C_t)V}{m}$$

Where C_o (mg/L) and C_t are the concentration in the solution at time t=0 and at time, t, V is the volume of solution (L) and m is the amount of adsorbent (g) added [3].

2.6 Effect of initial solution pH

The pH of the adsorbate solutions has been identified as the single most important parameter governing adsorption on different adsorbents. In order to determine when the maximum metal uptake occurs, a pH test will be performed. The pH of the solution is adjusted with dilute HCl or NaOH solution. The quantity of adsorbed zinc will be calculated from the following equation:

$$\% \text{ adsorbed} = \left(\frac{C_o - C}{C_o}\right) \times 100$$

Where C_o is initial concentration and C final zinc concentration in solution respectively [3].

2.7 Process of Producing Activated Carbon

Activated carbon can be produced by either physical or chemical activation, both of which require the use of elevated temperature

2.7.1 Physical activation: The carbonized material is mixed with gases at high temperature to activate it. The source material can be several carbonic materials, e.g. coconut shell, nutshells, wood, coal. It's also generally done by using one or combining carbonization and activation/oxidation process. *Carbonization* process happened when the material with carbon content is pyrolysed at temperatures in the range 600-900 °C, in absence of air while *Activation/Oxidation* happened when raw material or carbonized material is exposed to oxidizing atmospheres (carbon dioxide, oxygen, or steam) at temperature range 600-1200 °C.

2.7.2 Chemical activation: Impregnation with chemicals such as acids like phosphoric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride, followed by carbonization at temperatures in the range 450-900°C. It is believed that the carbonization / activation step proceeds simultaneously with the chemical activation. This technique can be problematic in some cases because, for example, zinc trace residues may remain in the end product. However, chemical activation is preferred over physical activation owing to the lower temperatures and shorter time needed for activating material. [4].

2.8 Definition of characterization

Characterization of a heterogeneous catalyst refers to the measurement of its 'characteristics' i.e. of those physical and chemical properties of the catalyst assumed to be responsible for its performance in a given reaction.

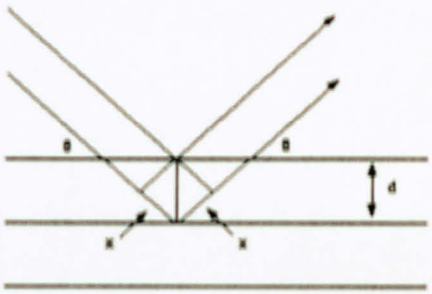
Physical properties include surface area, porosity, particle size and density. While chemical properties refer to metal dispersion, phase reducibility and acid sites.

2.8.1 Characterization techniques

2.8.1.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is used to reveal the chemical structural changes associated with the sorption process. XRD is the powerful tool for the characterization of bulk crystal structure and chemical phase composition by diffraction of an X-ray beam as a function of the angle of the incident beam. The principle of this technique is that crystal structures possess planes made by repetitive arrangements of atoms, which are capable of diffracting X-rays. [10]

Figure 2: Reflection of x-rays from two planes of atoms in a solid



Bragg Equation [10] is

n x wavelength = 2 d Sin (θ)

2.8.1.2 Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) used to measure the quantity and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere. Measurements are used to determine the composition of materials and to predict their thermal stability at temperatures up to 1000°C. The technique can characterize materials that demonstrate weight loss or gain due to

decomposition, oxidation, or dehydration.Facts like thermal stability of materials, oxidative stability of materials, composition of multi-component system, decomposition kinetics of materials, effects of reactive or corrosive atmospheres on materials and finally moisture and volatiles content of materials can be found by using TGA [11].

2.8.1.3 Scanning Electron Microscope (SEM)

Conventional light microscopes use a series of glass lenses to bend light waves and create a magnified image. SEM creates the magnified images by using electrons instead of light waves. The SEM shows 3-dimensional images at much higher magnifications. The images are very detailed. The images created without light waves are rendered black and white [12].

It can be used to estimate the pore size of the activated carbon quantitatively. Pore entrances, clearly visible as dark irregular shapes on lighter membrane background [13].

2.8.1.4 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDX) is used to identify the elemental composition of as little as a cubic micron of material. When a person is doing a study about elemental information of a certain specimen, it is often attached to the Scanning Electron Microscope (SEM).

EDX works by detecting X-rays that will be produced by a sample placed in an electron beam. The electron beam excites the atoms in the sample that later produce X-rays to release the excess energy. The energy of the X-rays is characteristic of the atoms that produced them, forming peaks in the spectrum. Individual elements can have more than one peak related to them and some peaks from different elements may overlap to a certain degree [14].

2.8.1.5 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 3: Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is a tool that recognizes types of functional groups in a molecule [5]. It is by producing an infrared absorption spectrum that is like a molecular "fingerprint". FTIR is used to identify chemicals that are either organic or inorganic. By interpreting the infrared absorption spectrum, the functional groups in a molecule can be determined. FTIR spectra of pure compounds are so unique that they are called a molecular "fingerprint". Organic compounds have very rich, detailed spectra where else inorganic compounds are usually much simpler [15].

Bonds and groups of bonds vibrate at specific frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are specific to that molecule. FTIR spectroscopy does not require a vacuum condition since neither oxygen nor nitrogen can absorb infrared rays. FTIR analysis can be applied to small quantities of materials, whether solid, liquid, or gaseous. The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface. Knowledge on surface functional groups would give insight to the adsorption capability of the produced activated chars. FTIR spectra are collected for qualitative characterization of surface functional groups of porous carbons activated by both physical and chemical methods [16].

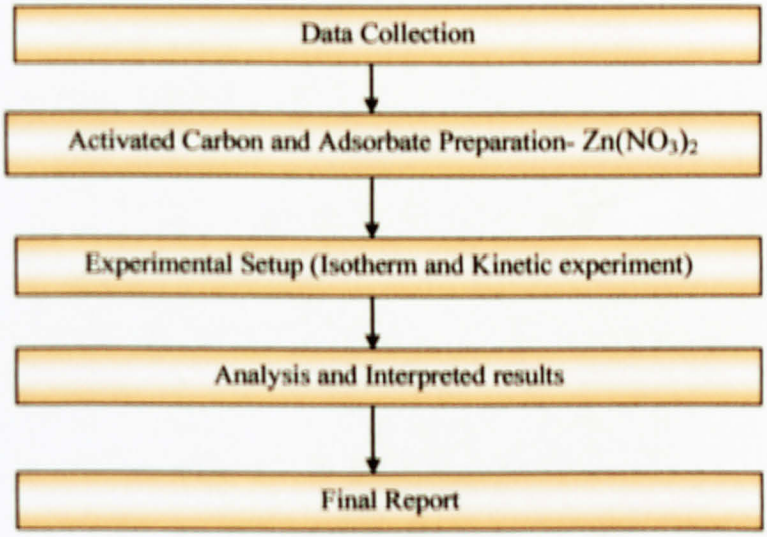
CHAPTER 3

METHODOLOGY

3.1 Project Work Flow

Before proceeding with the experiment itself, steps were drawn out diagrammatically to ensure the project flow is smooth and accomplish in the given period.

Figure 4: Flowchart of Project Work Flow



3.2 Chemicals used

i. Zinc nitrate ,$Zn(NO_3)_2$

ii. Sodium Hydroxide (NaOH)

iii. Activated Carbon prepared from coconut coir

iv. Hydrochloric Acid HCl

v. Sodium Bicarbonate (Na_2CO_3)

3.3 Tools/Equipments

i. 100ml Bottle sample, 1000ml Volumetric flask

ii. Graduated cylinder

iii. Rotary shaker, electronic balance

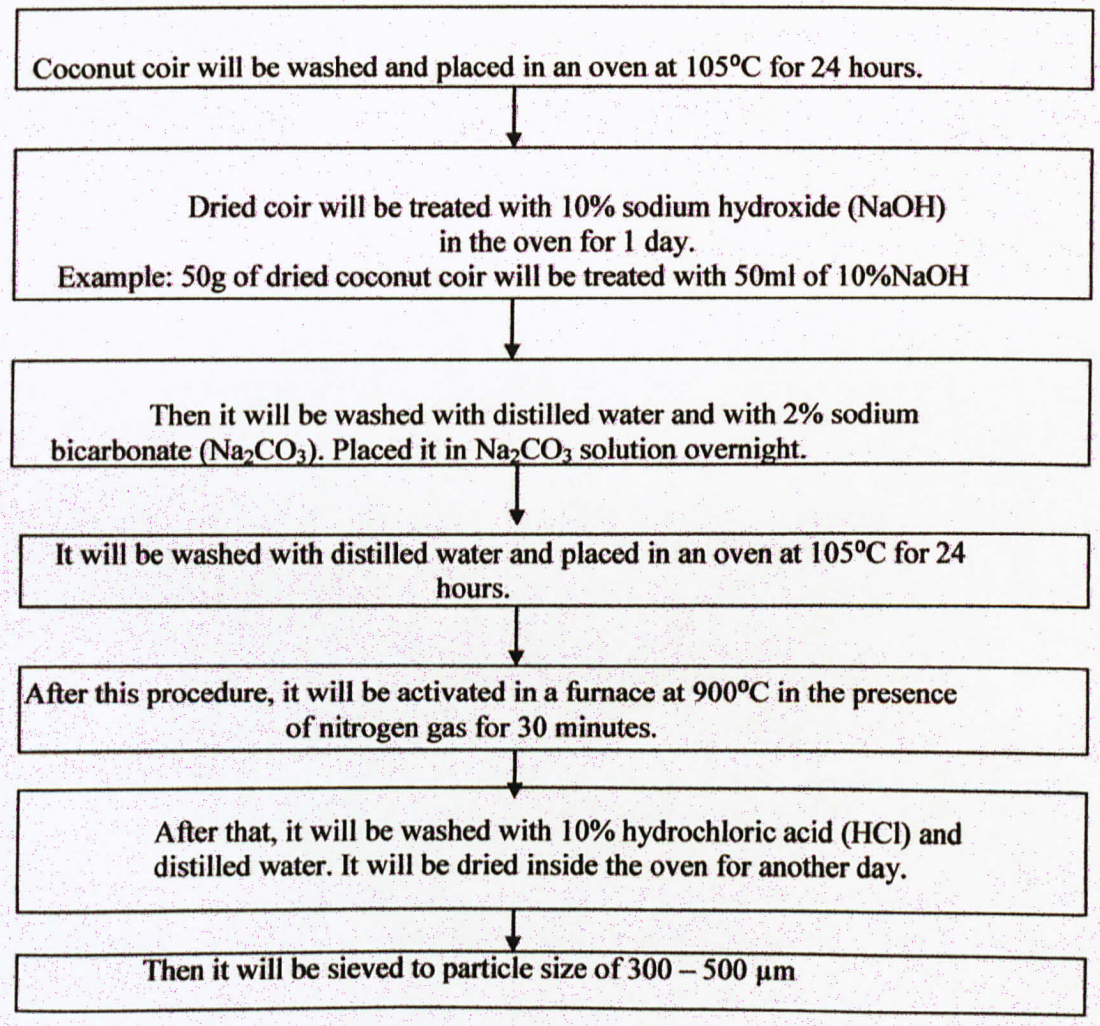
iv. Syringe Filter, pH meter

v. Atomic Adsorption Spectrophotometer (AAS) and Furnace

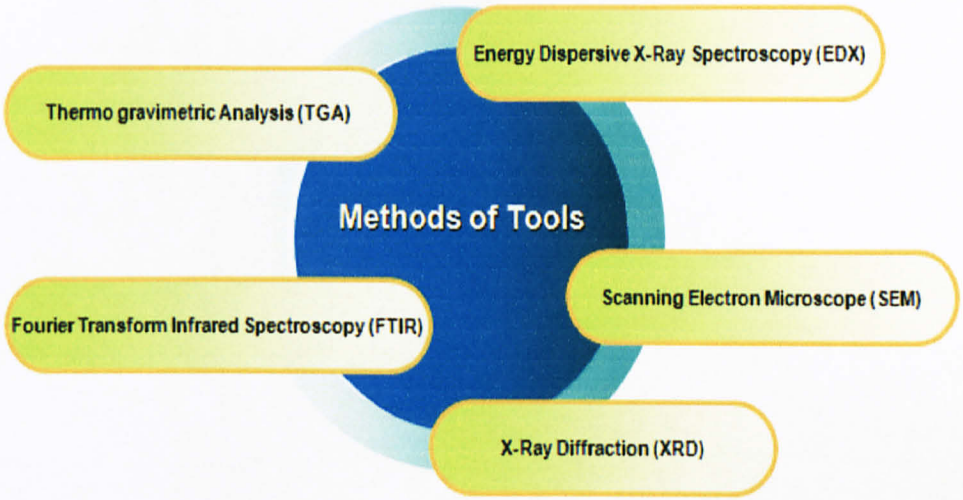
vi. FTIR, EDX, XRD, SEM & TGA

3.4 Method of Experiments

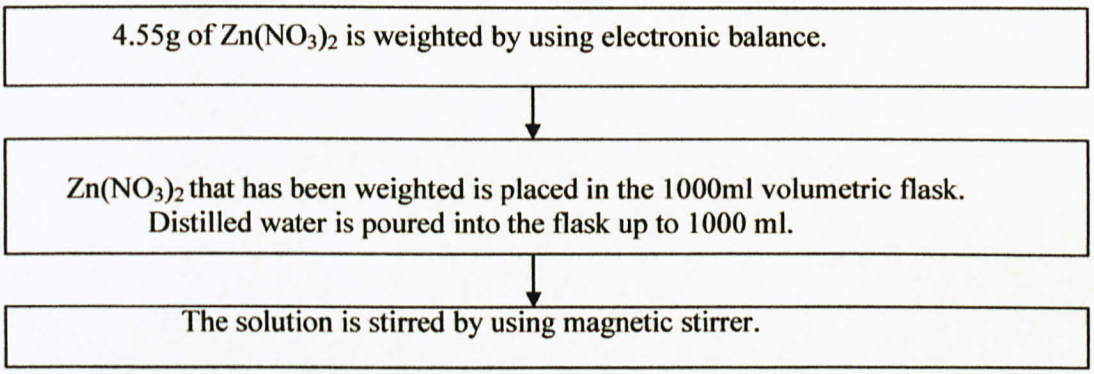
3.4.1 Preparation of activated carbon



3.4.2 Characterization of the activated carbon



3.4.3 Preparation of 1000 ppm of zinc solution, $Zn(NO_3)_2$



Stock zinc solution (1000ppm) is prepared by dissolving 4.55g of $Zn(NO_3)_2$. Standard solution of particular Zn(II) concentration was prepared by proper dilution with 1000 mL of distilled water.

3.4.4 Isotherm Experiments

Three bottle samples of 100 ml $Zn(NO_3)_2$ solutions are prepared by using the standard solution (1000 ppm) at the following concentrations:
Concentrations: 5 ppm, 10 ppm, and 20 ppm
(Note: Use $m_1v_1=m_2v_2$)

↓

At time zero, 0.2 g of granular activated carbon is added to the respective bottle sample.

↓

The bottle samples are covered with aluminum foil and placed over rotary shaker and shaken at 150 rpm at room temperature.

↓

5 ml samples are taken using syringe filter at known time intervals and sampling is continued until the product analysis attains the equilibrium condition.

↓

The remaining concentration of $Zn(NO_3)_2$ in each sample are filtered using syringe filter and analyzed using atomic adsorption spectrophotometer (AAS)

The adsorption isotherm is conducted by added 0.2g coconut coir activated carbon to bottle sample containing 100ml of zinc solution. The zinc concentration was varied for 5ppm, 10ppm and 20 ppm. The remaining concentration of Zn(II) in each sample after adsorption at different time intervals is determined by atomic-absorption spectroscopy after filtering the adsorbent with 0.45µm syringe filter to make it carbon free.

3.4.5 Batch Kinetic Experiment

3.4.5.1 Effect of initial metal ion concentration

Three bottle samples of 100 ml $Zn(NO_3)_2$ solutions are prepared by using the standard solution (1000 ppm) at the following concentrations:
Concentrations: 5 ppm, 10 ppm, and 20 ppm *(Note: Use $m_1v_1=m_2v_2$)*

↓

At time zero, 0.2 g of granular activated carbon is added to the bottle samples.

↓

The bottle samples are covered with aluminum foil and placed over rotary shaker and shaken at 150 rpm at room temperature.

↓

5 ml samples of each solution are withdrawn from the bottle samples using syringe filter at different time intervals. Contact time of x minutes will be used for batch tests.

(Note: Contact time can be determined from the isotherm experiments when the removal rate is negligible after that contact time)

↓

All samples are filtered and analyzed by using AAS

3.4.5.2 Effect of pH

100 ml of 20 ppm $Zn(NO_3)_2$ solution is placed in four bottle samples.

↓

At time zero, 0.2 g of adsorbent is added into the bottle sample.

↓

pH values of solution is ranging from 3.0 to 6.0 by adjusting with 0.5M HCl and NaOH solutions. The solution is placed over rotary shaker and shaken at 150 rpm, at 25^0C. The pH was measure using a pH meter.

(Note: pH can be increased by adding NaOH while to decrease the pH, HCl must be added to the solution)

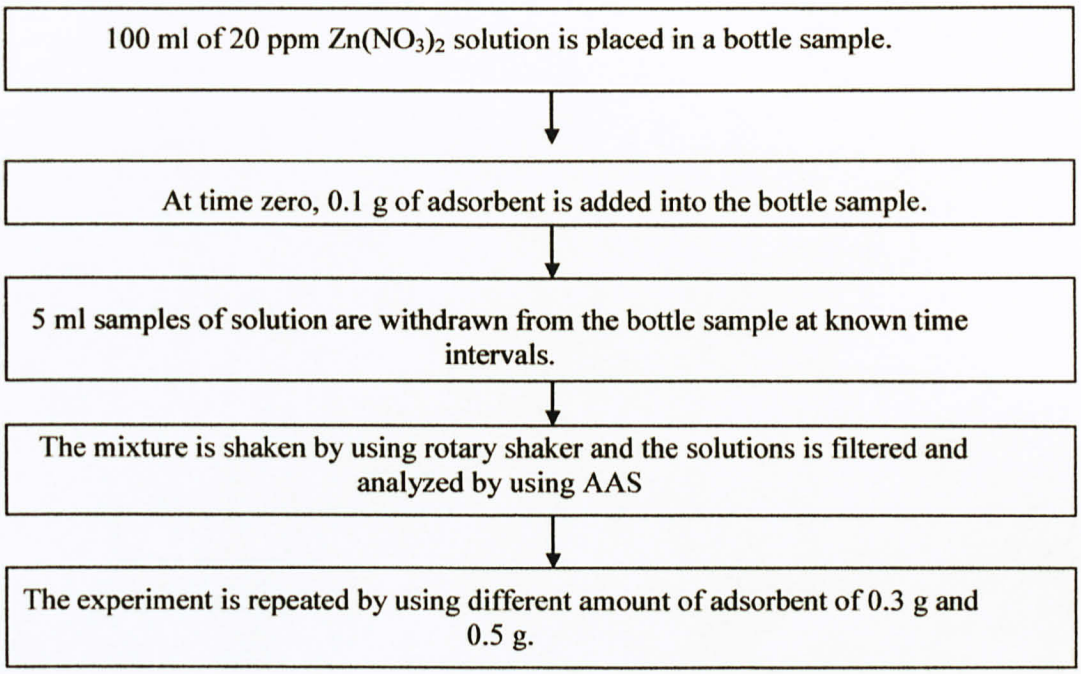
↓

5 ml samples of solution are withdrawn from the bottle samples using syringe filter at known time intervals.

↓

The mixture is shaken by using rotary shaker and the solutions is filtered and analyzed by using AAS.

3.4.5.3 Effect of Adsorbent Dosage



CHAPTER 4

RESULT AND DISCUSSION

4.1 Activated Carbon Preparation

Figure below shows the dried coir was treated with 10% sodium hydroxide (NaOH) and with 2% Sodium Bicarbonate ($NaHCO_3$) during the preparation of activated carbon.

Figure 5: (a) 10% NaOH) was poured into the dried coconut coir
(b) Coconut coir that had been washed with ($NaHCO_3$).

(a)

(b)

At the last stage of preparing AC, Fixed Bed Activation Unit (FBAU) had been used to activate the AC. The AC was placed in that furnace at 900°C for 30 minutes. The amount of the AC lost during the activation process is about 50%-60%. Nitrogen gas is supplied to the activation unit at flow of 0.15 (150ml/min) and the sample is taken out when temperature is less than 100°C.

Figure 6: Fixed Bed Activation Unit (FBAU) used to proceeds simultaneous physical and chemical activation at temperatures 600-900°C.

Figure 7: Dried coconut coir before it is placed in FBAU.

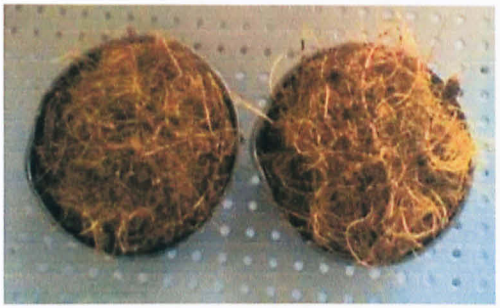
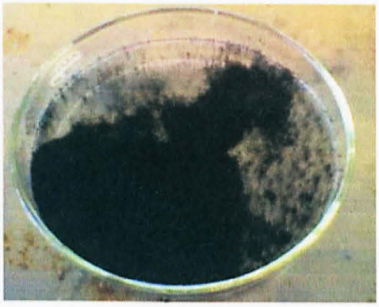


Figure 8: Activated carbon produced after undergo the activation process

Figure 9: Activated carbon after it was sieved to small particle size of 500 μm.

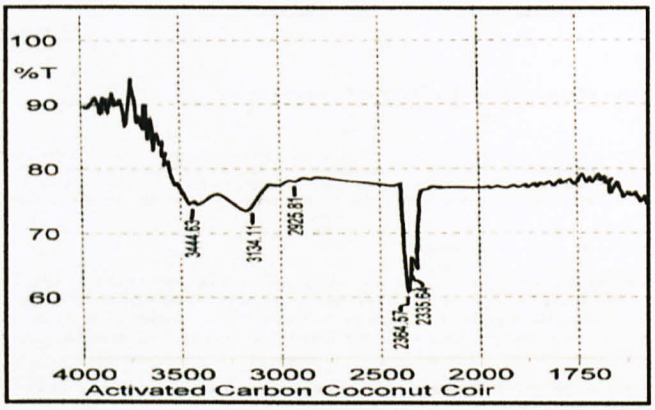


During activation process in Fixed Bed Activation Unit (FBAU), the internal surface of activated carbon (coconut coir) becomes more highly developed and extended by controlled oxidation of carbon atoms, usually achieved by the use of steam at high temperature. The internal surface area must be accessible to the passage of a fluid or vapor if a potential for adsorption is to exist. Thus, it is necessary that an activated carbon has not only a highly developed internal surface but accessibility to that surface via a network of pores of differing diameters. The carbonization and activation were carried out at 900 °C under N_2 gas flow for 1/2 hour. The resulting activated carbon was washed with 10% HCl followed by distilled water until traces of chloride ions were no longer detected and then stored in plastic bottles for further use.

4.2 Characterization of the activated carbon

4.2.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 10: FTIR spectrum of activated carbon.

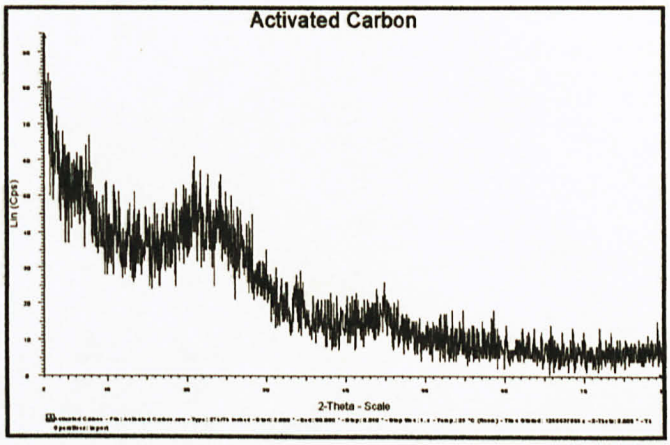


A quantitative analysis of activated carbon was conducted by obtaining FTIR transmission spectra of carbon samples. The adsorption capacity of activated carbon depends upon porosity as well as the chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between forces at the surface as compared to those within the body, thus leading to molecular adsorption by the van der Waals force. Knowledge on surface functional groups would give insight to the adsorption capability of the produced activated chars. FTIR spectra were collected for qualitative characterization of surface functional groups of porous carbons activated by both physical and chemical methods. Figure 10 shows the functional groups of activated carbon prepared from coconut coir.

The FTIR spectrum of coconut coir AC reveals a broad peak at 3444.63 cm^{-1} and 3134.11 cm^{-1} which can be attributed to the O-H group. The peak observed at 2925.81 cm^{-1} corresponds to the C-H stretching group. The alkynes group of C≡C is found around 2364.57 cm^{-1} to 2335.64 cm^{-1}.The vibration at 1400.22 cm^{-1} is assigned to the alkanes group of C-H. The peaks from 1035.70 cm^{-1} to 1035.70 cm^{-1} are assigned to the carbonyl stretching group, C-OH stretching in primary alcohol (1035.70 cm^{-1}) and secondary alcohol (1107.36 cm^{-1}).

4.2.2 X-ray Diffraction (XRD)

Figure 11: X-ray diffractogram of AC prepared from coconut coir



The crystal structure characteristics of the result samples were analyzed by x-ray diffractometer (XRD) as a radiation source. The measurement was carried out in a scale 2θ and long duration scan 15s. The x-ray diffraction patterns of activated carbon sample are shown in figure above. From the figure, a broad peak existed at 2θ = 7 ° and 22° with relative intensity of 58 to 65 cps for coconut coir correspond to the lattice plane cellulose. Reasonably, the peaks for the coconut coir increased with density which is commonly observed in nanosized carbon. The sharp lines superimposed on the broad carbon peaks above 2θ of 22° are identified as silica, perhaps unavoidable impurity in activated carbon [17]. When the activated carbon of coconut coir is treated with acids (HCl), the majority of those peaks were completely absent due to leaching out the corresponding minerals during activation and washing with water. It will removed significant amount of mineral matter present in the plant tissues which remain intimately bound with carbon material such as removal of alkali (Na, K), alkaline (Ca, Mg) and transition (Fe) metals which are inevitable in the coconut coir from lignocellulosic materials. Reasonably, the peaks for the coconut coir increased with density which is commonly observed in nanosized carbon.

The cell walls of most of the natural fibers mainly consist of cellulose, hemicellulose, and lignin. Cellulose has both amorphous and crystalline regions, although hemicellulose and lignin are amorphous. Thus the main function of lignin is to impart strength and rigidity

to the cell wall by acting as structural matrix. The intensity of the peaks did change, suggesting differences in crystallinity and also their crystallite size depend on the heat treatment. The XRD pattern of activated carbon fiber shows almost no diffraction lines and is confirmed to be the amorphous material [18]. The XRD pattern of result sample after synthesis shows the diffraction lines corresponding to cellulose in a face centered cubic structure.

Due to their thinness (or small "crystallite size") and the polycrystalline morphology of the coconut coir, their x-ray diffraction diagrams do not exhibit sufficiently detailed diffraction data to permit a full structure analysis to be completed, such as can be done with large single crystals [19]. The relative low temperature allows the formation of small amounts of stable structure which is evidenced by the peak located at around diffraction angle of 50°. In addition to the diffraction lines, a broad peak at low diffraction angles is observed corresponding to the presence of amorphous phase in the sample [20]. That could be attributing to the unreacted remaining carbon.

4.2.3 Scanning Electron Microscope (SEM)

Figure 12: Images of long pieces of raw coconut coir

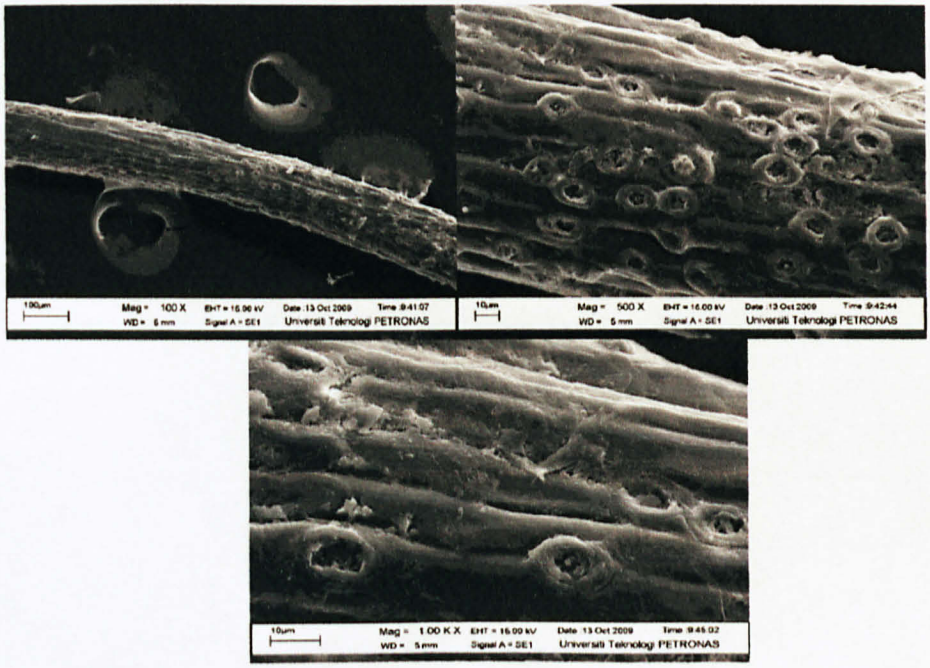


Figure 13: Images of small dust of raw coconut coir

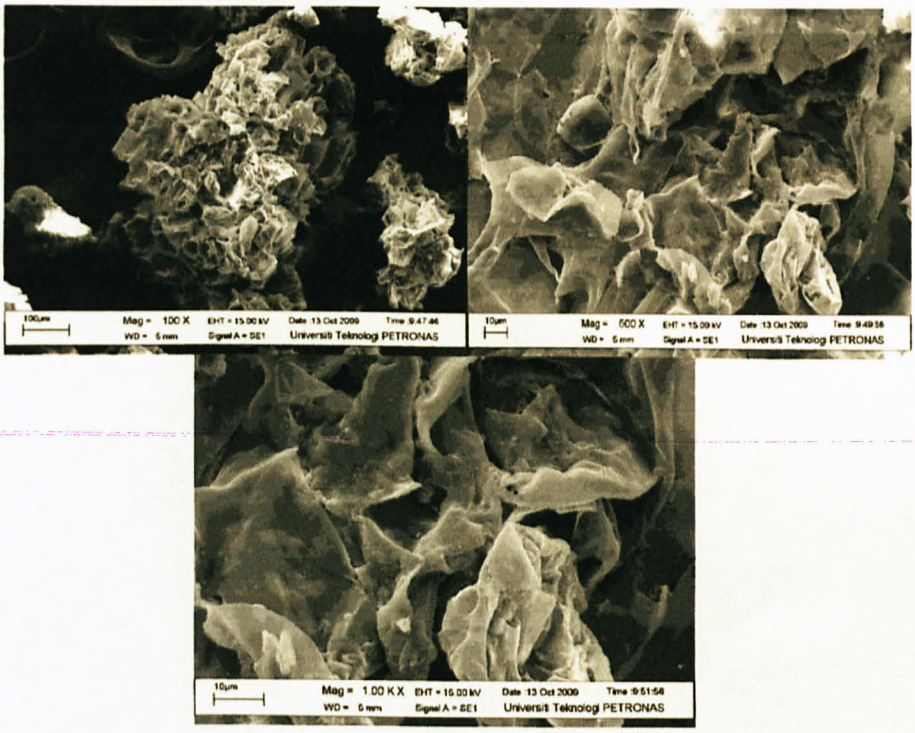


Figure 12 and Figure 13 are the images of raw coconut coir that have not undergone any chemical reaction. There 2 parts of the coir that had been analyzed. The parts are from the long pieces of the coir and the small dust of the coir. The images had been magnified for 100, 500 and 1000 times. The images showed that there are quite a number of small pores that is important for adsorption. In Figure 12, there are small pores but number is very little. Meanwhile, Figure 13 showed the structure of the dusts that are not uniform. There are also lots of small pores or spaces inside the structure.

Figure 14: Images of long pieces of the activated carbon

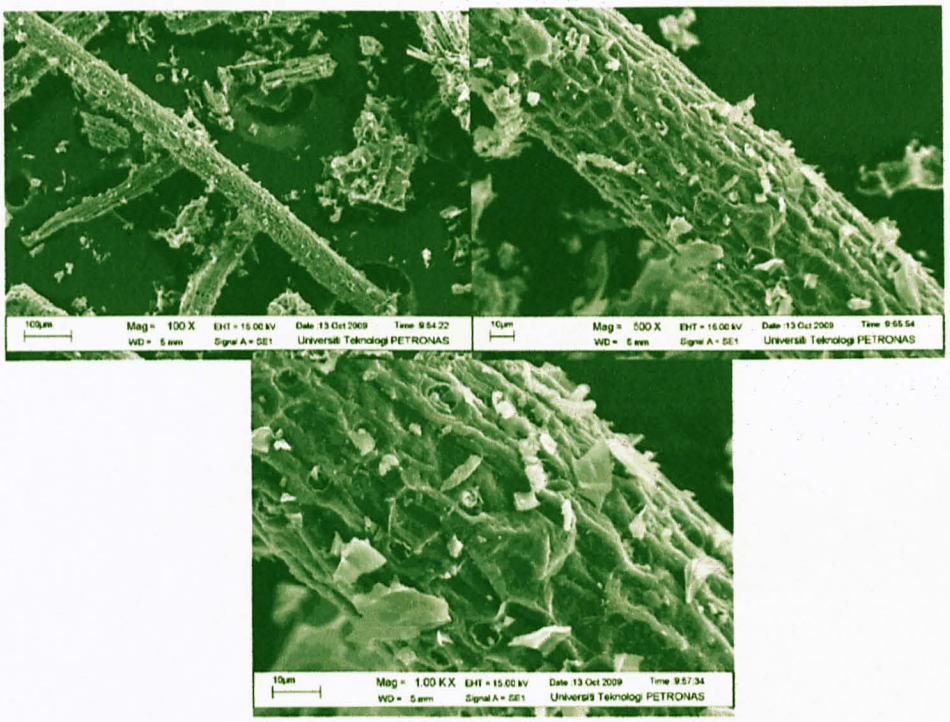


Figure 15: Images of small dust of the activated carbon

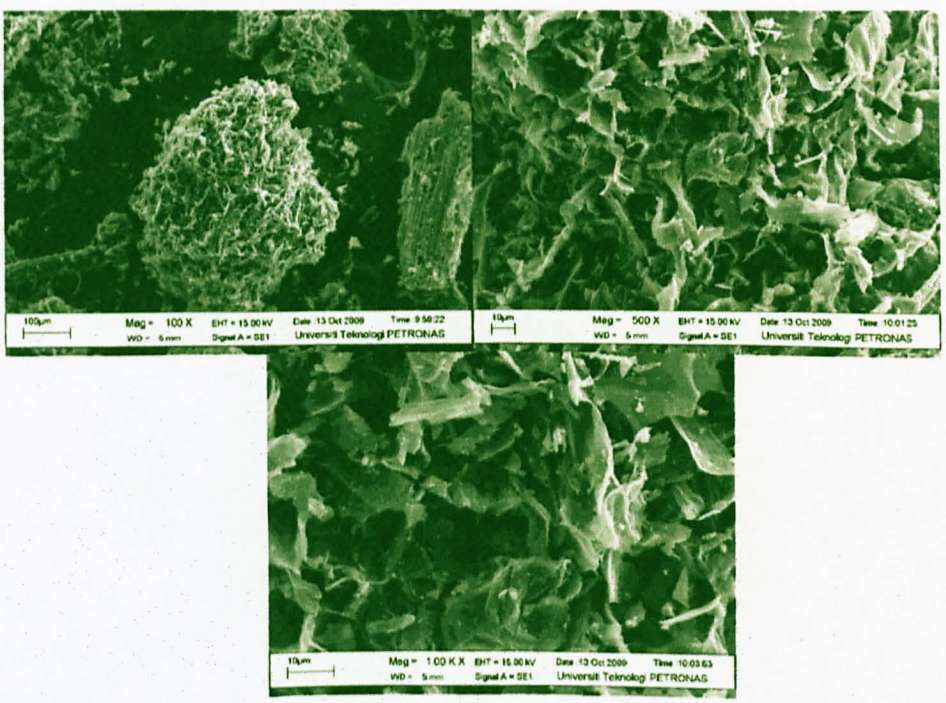


Figure 14 and Figure 15 showed the structure of the coconut coir that had been converted into activated carbon. The number of pores of the coconut coir had been increased after the chemical and physical activation. These images showed that the ability of the coir to adsorb is higher due to higher number of pores. The structures had become more complex. Much more "chamber" like structure had been formed. Thus it will increase the capacity of adsorption.

4.3 Adsorption Experiments

4.3.1 Effect of Initial Metal Ion Concentration Experiment

Figure 16: Effect of initial metal ion concentration on Zn (II) adsorption by coconut coir

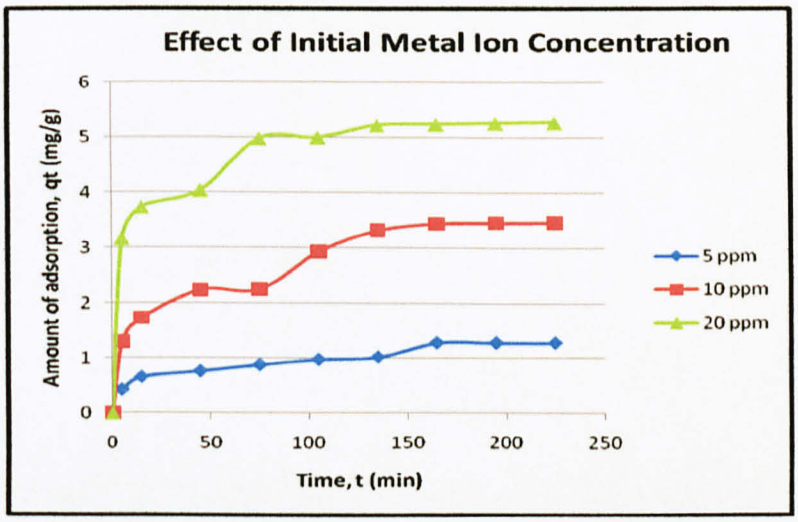
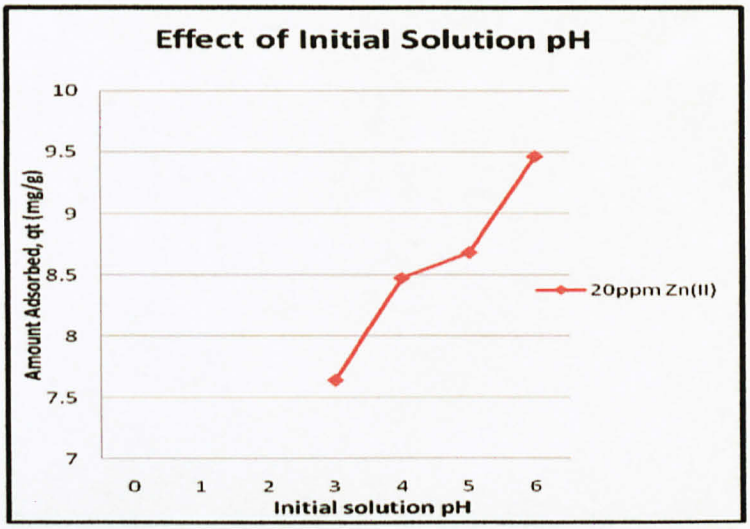


Figure 16 shows amount of adsorption, qt (mg/g) as function of time for range of zinc ion concentration. It was observed that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at each initial metal ion concentration and equilibrium is attained within about 165 min for the systems. Further, it was observed that the amount of metal ion uptake, q_t (mg/g) is increased with increase in initial metal ion concentration. At high ion concentration, the ratio of surface active sites to the total metal ions in the solution is high and hence all metal ions may interact

with the adsorbent and will be remove from the solution. This increase in loading capacity of the sorbent with relation to the metal ions concentration can be explained with the high driving force for mass transfer. In fact, the more concentrated the solution is the better the adsorption. Equilibrium adsorption isotherms relate the adsorbate concentration in the bulk and the adsorbed amount on the interface. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for design purposes.

4.3.2 Effect of Initial Solution pH

Figure 17: Effect of initial solution pH on Zn (II) adsorption by coconut coir



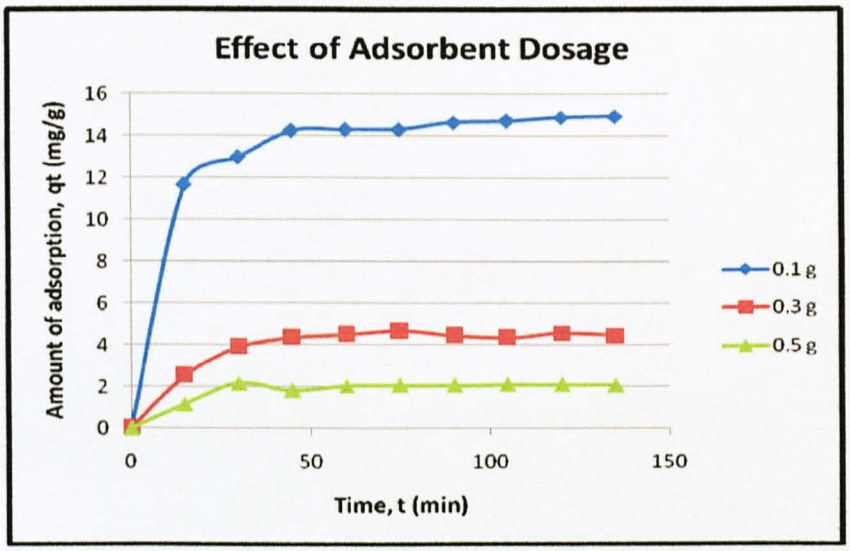
The pH of the adsorbate solutions has been identified as the single most important parameter governing adsorption on different initial solution pH. The number of active sites on the surface of the adsorbent may change with varying pH. The adsorption capacities were found to be low at lower pH values and increased with increase in pH. This can be explained with competitive adsorption of H+ ions and metal ions for the same active adsorption site. As the pH increased, the adsorption surface becomes less positive and therefore electrostatic attraction between the metal ions and activated carbon surface is likely to be increased. This dependence of metal uptake on pH is related to the

functional group of coconut coir. The minimal adsorption at low pH is due to the higher concentration and high mobility of H^+, which are preferentially adsorbed than metal ion. At higher pH, the lower number of H^+ along with more negative charge coir gives greater metal ion adsorption.

The pH range was chosen as 3 to 6 in order to avoid precipitation of the metal ions, all of the experiments were carried out at a maximum initial solution pH of 6.0. The removal of metal ions was found to increase when the solution pH increased from 3.0 to 6.0 for the system.

4.3.3 Effect of Adsorbent Dosage

Figure 18: Effect of adsorbent dosage on Zn (II) adsorption by coconut coir



Adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage was studied on Zn(II) ion removal from aqueous solutions by varying the amount of activated carbon (0.1g, 0.3g, 0.5g) , while keeping other parameters (pH, agitation speed, temperature and contact time) constant. Figure 18 showed that the amount of Zn(II) ion adsorbed (qt) increased as the adsorption dosage was decreased from 0.1g,

0.3g and 0.5g. On the other hand, the amount adsorbed per unit mass of the adsorbent decreased considerably. The decrease in unit adsorption with increase in the dosage of adsorbent was due to adsorption sites remaining unsaturated during the adsorption process and may be due to the overlapping and aggregation of adsorption sites occurs as a result to overcrowding of adsorbent particles when dose increased from 0.1 to 0.5 g/100 ml. In addition, at higher amount of adsorbent used, the ion concentration drops to a lower value and the system reaches equilibrium at lower values of *'q'* indicating the adsorption sites remain unsaturated.

4.4 Adsorption Equilibrium Isotherm

The adsorption isotherm provides a relationship between the concentration of metal ions in solution and the amount of metal ions adsorbed onto the adsorbent when both phases are at equilibrium. The measured adsorption equilibrium data were fitted with Langmuir, and Freundlich isotherm equations within the metal ion concentration range of 5ppm to 20ppm. The Freundlich adsorption isotherm, which assumes that adsorption takes place on heterogeneous surfaces, can be expressed as [21];

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e)$$

Where q_e is the amount of metal ion adsorbed at equilibrium time, C_e is equilibrium concentration of zinc metal ion in solution. K_f and $1/n$ are isotherm parameters which indicate the capacity and the intensity of the adsorption respectively and can be calculated from the intercept and slope of plot between ln q_e and ln C_e. The isotherm data is fitted with the Freundlich model ($R_2 = 0.699$) shows in figure 19. The value of $1/n$ is less than 1 indicates a favourability of adsorption. The Freundlich equation frequently gives an adequate description of adsorption data over a restricted range of concentration, even though it is not based on the theoretical background. Apart from homogenous surface, the Freundlich equation is also suitable for a highly heterogonous surface and an adsorption isotherm lacking a plateau, indicating a multi-layer adsorption.

According to Langmuir model, adsorption occurs uniformly on the active sites of the adsorbent and once an adsorbate occupies a site, no further adsorption can take place at this site. Therefore Langmuir isotherm equation was tested with this same metal ion concentration range. The linearized form of Langmuir can be written as [22];

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$$

The Langmuir constants, q_m (maximum adsorption capacity) and K_a (values for Langmuir are predicted from the plot between $1/q_e$ versus $1/C_e$ shows in figure 20.

The correlation coefficient, R^2 was also tabulated to indicate the closeness of the fit. Therefore, the isotherm study indicated that adsorption data correlated well with Freundlich isotherm model.

Figure 19: Freundlich adsorption isotherm

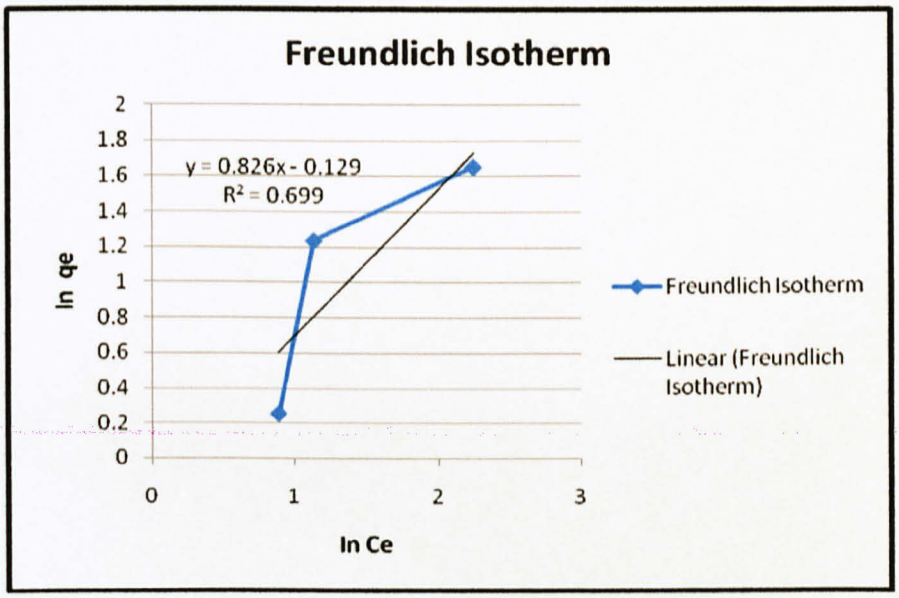
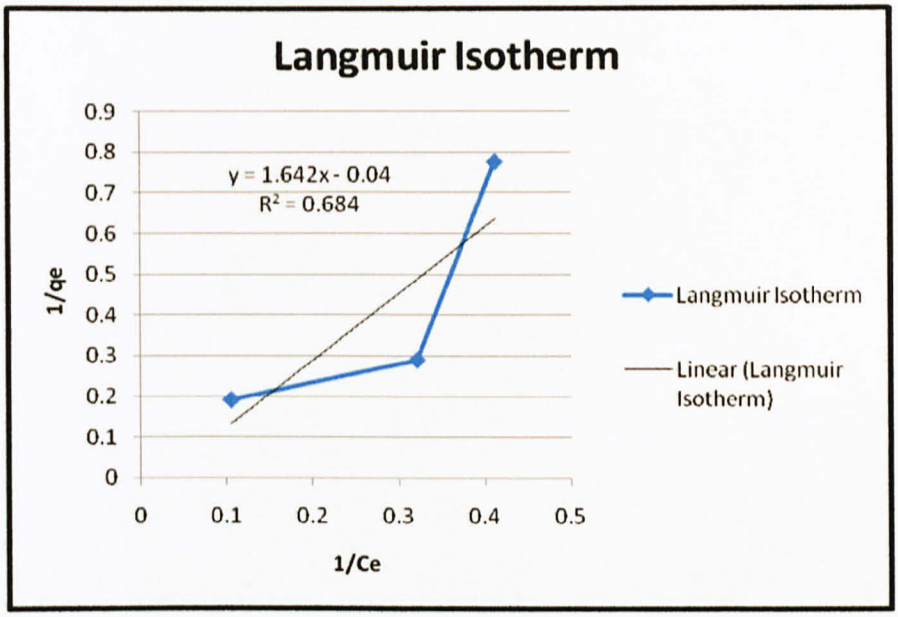


Figure 20: Langmuir adsorption isotherm



CHAPTER 5

CONCLUSION

The results obtained in this study clearly demonstrated that coconut coir from agriculture by-products can be considered as a low cost potential good adsorbent for the removal of zinc ions from aqueous solution. The following conclusions can be drawn based on these three investigations;

First, the adsorption characteristic of zinc metal ion is strongly affected by initial solution pH, initial metal ion concentration and amount of adsorbent respectively. In a batch adsorption studies, the amount of metal ion adsorption on coconut coir increases with initial metal ion concentration, solution pH but decrease with the amount of adsorbent.

Second, it has also been found that the amount of adsorption i.e. mg of adsorbate per gram of adsorbent increases with increasing contact time at all initial metal ion concentrations and equilibrium is attained within 180 minutes for Zn-coconut coir systems at a fixed solution pH. pH is one of the important parameters for metal ion adsorption on coconut coir and it has been found that zinc adsorption increases with increasing pH of the solution.

Third, Langmuir and Freundlich equations are used to describe the adsorption of zinc metal ion on coconut coir within this initial metal ion concentration range. The isotherm study indicated that adsorption data correlated well with Freundlich isotherm model. This study demonstrated that the coconut coir could be used as an effective adsorbent or neutralizing agent for the treatment of wastewater containing zinc ions. Besides that, adsorbent being composed entirely by very low prizes agricultural waste and that waste is not put to any other use. It helps to reduce the cost of waste disposal and provide an alternative adsorbent to the existing commercial activated carbon.

RECOMMENDATION

1) For further study, the activated carbon can be prepared by varying the use of chemical for activation at different temperature.

2) This technique can be applied in wastewater treatment for heavy metals removal.

3) Compare the effect between chemical activation and thermal activation in preparing the activated carbon.

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APPENDICES

Table 1: AAS data for Effect of Initial Metal Ion Concentration

	Initial Zinc Concentration (Co),ppm	5		10		20
Time (min)	Zinc remaining concentration (Ct) ,ppm	Amount adsorbed,qt (mg/g)	Zinc remaining concentration (Ct) ,ppm	Amount adsorbed,qt (mg/g)	Zinc remaining concentration (Ct) ,ppm	Amount adsorbed,qt (mg/g)
0	5	0	10	0	20	0
5	4.1283	0.43585	7.4114	1.2943	13.6724	3.1638
15	3.6811	0.65945	6.547	1.7265	12.5337	3.73315
45	3.4653	0.76735	5.5234	2.2383	11.9206	4.0397
75	3.2351	0.88245	5.4923	2.25385	10.0532	4.9734
105	3.043	0.9785	4.1245	2.93775	10.0083	4.99585
135	2.9501	1.02495	3.3611	3.31945	9.5613	5.21935
165	2.4253	1.28735	3.1098	3.4451	9.5242	5.2379
195	2.4231	1.28845	3.0776	3.4612	9.4799	5.26005
225	2.4198	1.2901	3.0581	3.47095	9.4548	5.2726

Table 2: AAS data for Effect of Initial Solution pH

	Initial Zinc Concentration (Co),ppm	20
Initial solution pH	Zinc remaining concentration (C) ,ppm	Amount adsorbed,qt (mg/g)
0		
1		
2		
3	4.7291	7.63545
4	3.0501	8.47495
5	2.6479	8.67605
6	1.0643	9.46785

Table 3: AAS data for Effect of Adsorbent Dosage

	Amount of adsorbent	0.1g		0.3g		0.5g
Time (min)	Zinc remaining concentration (C) ,ppm	Amount adsorbed (mg/g)	Zinc remaining concentration (C) ,ppm	Amount adsorbed (mg/g)	Zinc remaining concentration (C) ,ppm	Amount adsorbed (mg/g)
0	20.000	0	20	0.0000	20	0
5	8.3421	11.6579	12.4057	2.5314	14.304	1.1392
15	7.0397	12.9603	8.3214	3.8929	9.1779	2.16442
45	5.7617	14.2383	6.9715	4.3428	11.046	1.7908
75	5.7011	14.2989	6.5931	4.4690	9.9003	2.01994
105	5.6810	14.3190	6.0802	4.6399	9.8292	2.03416
135	5.3493	14.6507	6.7074	4.4309	9.8085	2.0383
165	5.2741	14.7259	6.9948	4.3351	9.5906	2.08188
195	5.1085	14.8915	6.3455	4.5515	9.5676	2.08648
225	5.0459	14.9541	6.6541	4.4486	9.7248	2.05504

Table 4: Freundlich experimental value

Concentration	Ce	qe	ln qe	ln Ce
5 ppm	2.425	1.28735	0.252586	0.885955
10 ppm	3.110	3.445	1.236953	1.134558
20 ppm	9.524	5.238	1.655921	2.253836

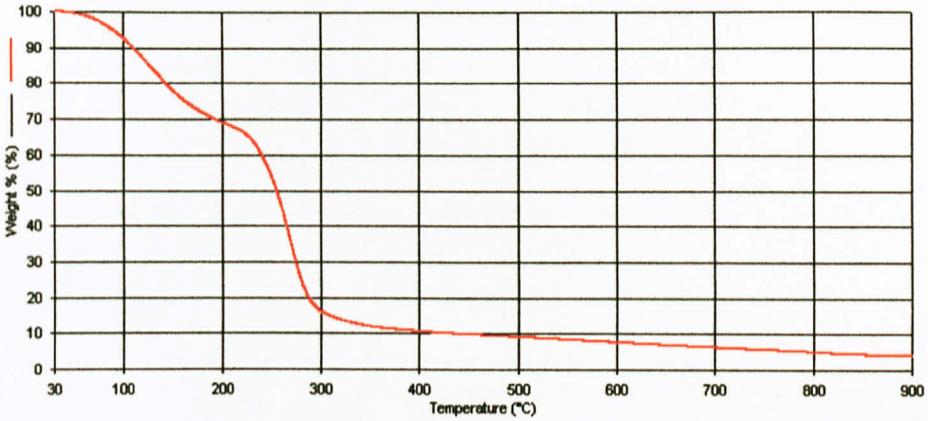
Freundlich:

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e)$$

Table 5: Langmuir experimental value

Concentration	Ce	qe	1/qe	1/Ce
5 ppm	2.425	1.28735	0.77679	0.41232
10 ppm	3.110	3.445	0.290267	0.321564
20 ppm	9.524	5.238	0.190916	0.104996

TGA Result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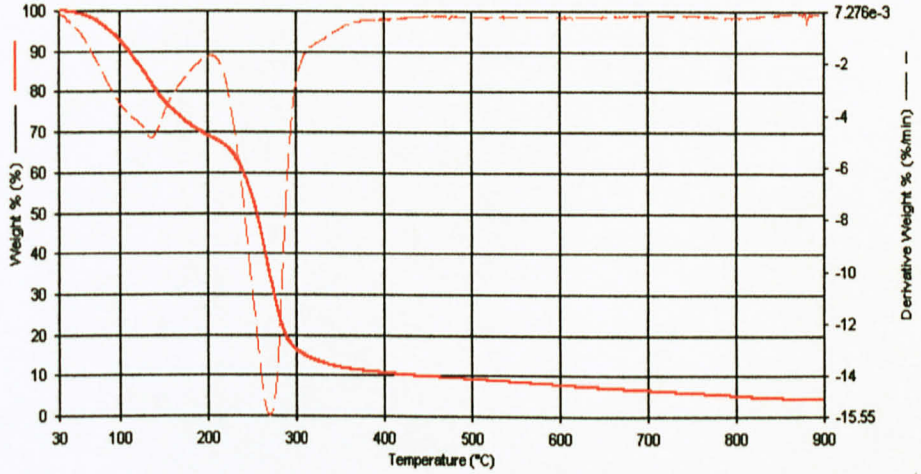
Temperature (°C)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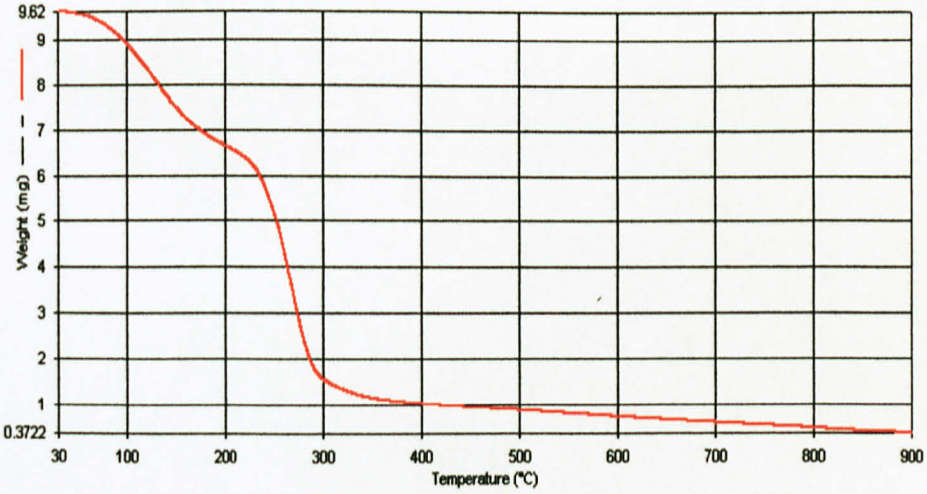
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